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Standard Entropies of Compounds: Theoretical Aspects of Latimer's Rule

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Latimer (1921) and others have suggested empirical formulas for the standard entropy $S^0 = S(298\text{ K})$ of solid compounds. Without any rigorous theoretical analysis, they assume that the explicit dependence on the constituent atomic masses M_i $(1 \leqslant i \leqslant j)$ is given by $c_1 \ln M_1 + \cdots + c_j \ln M_j$, where c_i is the concentration of the atom of kind i $(0 < c_i < 1)$. It is shown, from lattice dynamical theory, that this is the correct mass dependence for the high temperature limit of the vibrational entropy. Thus, it is correct in an estimate of S^0 provided that the masses M_j are not too small and the interatomic forces not too strong.

KEY WORDS: entropy; Latimer's rule; lattice dynamics; lattice vibrations.

1. INTRODUCTION

The standard entropy $S^0 = S(298.15\text{ K})$ of solids is an important thermophysical quantity, and there are several methods to estimate S^0 in the absence of measurements [1]. One of these, which is still frequently used, was suggested by Latimer [2] in 1921. Guided by how the mass appears in the classical entropy of gases, he postulated that S^0 of elemental solids varies only with the atomic mass M, and is of the form

$$S^0 = (3R/2)\ln M + Rs' \tag{1}$$

per mole. He also postulated that S^0 of a compound is the sum of contributions from each atom, which are independent of the specific

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compound and given by Eq. (1). As an example, S^0 for the compound A_mB_n would be (per mole)

$$S^0 = (3R/2)(m \ln M_A + n \ln M_B) + R(m+n)s' \tag{2}$$

The constant s' was determined empirically by Latimer, from S^0 of KCl. In an improved version, Latimer [3] adjusted Eq. (1) for positive ions to allow for size effects, but since the size of an ion was assumed to scale with the mass, S^0 was still a function of mass only. The negative ions were assigned empirical entropies which varied with their charge.

Latimer's rule often gives S^0 to within 10% of the experimental value, which suggests that the rule is physically well founded. Closely related expressions have been used by, e.g., Eastman [4], Treadwell and Mauderli [5], Kaufman [6], Kelley [7], and Pitzer and Brewer [8]. Others, for instance, Wenner [9] and Cantor [10], have proposed formulas which explicitly contain the molecular weight [e.g., $\ln(mM_A + nM_B)$ instead of $m \ln M_A + n \ln M_B$]. None of these papers give an adequate theoretical discussion of the mathematical expression used to estimate S^0; such an analysis is provided here. It will show that Latimer's rule is implied under certain assumptions about the Debye temperature and the invariance of the interatomic forces.

2. SOME THEORETICAL RESULTS FOR HARMONIC LATTICE VIBRATIONS

The high temperature expansion of the vibrational entropy is [11]

$$\begin{aligned} S(T) &= k_B \int_0^{\omega_{\max}} \left[1 + \ln\left(\frac{k_B T}{\hbar\omega}\right) + \frac{1}{24}\left(\frac{\hbar\omega}{k_B T}\right)^2 + \dots \right] F(\omega)\, d\omega \\ &= 3rNk_B \left[1 + \ln\left(\frac{k_B T}{\hbar}\right) - \langle \ln\omega \rangle + \frac{1}{24}\left(\frac{\hbar}{k_B T}\right)^2 \langle \omega^2 \rangle + \dots \right] \end{aligned} \tag{3}$$

$F(\omega)$ is the phonon density of states (normalized to 3 per atom), r is the number of atoms in a formula unit of the compound, and rN is the total number of atoms in the sample. The quantities $\langle \omega^n \rangle$ are defined by

$$\langle \omega^n \rangle = \int \omega^n F(\omega)\, d\omega \Big/ \int F(\omega)\, d\omega \tag{4}$$

for $n > -3$. When $n = 0$, ω^n is replaced by $\ln\omega$ in Eq. (4), which defines

$\langle \ln \omega \rangle$. In a Debye model, $\langle (\hbar\omega)^n \rangle = ((3/n+3))(k_B\theta_D)^n$ and $\langle \ln(\hbar\omega) \rangle = \ln(k_B\theta_D) - 1/3$. Here θ_D is the Debye temperature.

Grimvall and Rosén [11] have derived a result for $\langle \ln \omega \rangle$ in terms of the constituent masses and the (mass independent) force constant part $D_0(\mathbf{q})$ of the dynamical matrix. One has

$$\langle \ln \omega \rangle = \frac{1}{6rN} \sum_{\mathbf{q}} \ln(\det D_0(\mathbf{q})) - \frac{1}{2} \ln M_e \tag{5}$$

M_e is an effective mass,

$$M_e = M_1^{c_1} M_2^{c_2} \ldots M_j^{c_j} \tag{6}$$

where M_i $(1 \leqslant i \leqslant j)$ are the masses of the j different atoms in the compound and c_i are the corresponding concentrations $(0 < c_i < 1)$. The first term on the rhs of Eq. (5) is an average of the logarithm of interatomic forces. We call this term $\ln \beta$ and get

$$\langle \ln \omega \rangle = \ln \beta - \frac{1}{2} \ln M_e \tag{7}$$

3. THEORETICAL JUSTIFICATION FOR LATIMER'S RULE

With $\langle \ln \omega \rangle$ from Eq. (6), and $T = T' = 298.15$ K, expression (3) gives

$$S^0 = (3rR/2)\ln M_e + 3rR\left[1 + \ln(k_B T'/\hbar\beta)\right]$$
$$+ (3rR/24)(\hbar/k_B T')^2 \langle \omega^2 \rangle + \cdots \tag{8}$$

per mole of the compound. If the last term can be neglected, and if the average effective interatomic force constant (or equivalently $\ln \beta$) is the same for all compounds, Eq. (8) is exactly equivalent to Latimer's rule from 1921.

To elucidate the first of these conditions we assume a Debye model. Then the first two terms of $S^0/(3rR)$ from Eq. (3) give $4/3 + \ln(T'/\theta_D)$. The next term, $(1/40)(\theta_D/T')^2$, is less than 6% of $4/3 + \ln(T'/\theta_D)$ if $\theta_D < 3T'/2$, but rapidly increases in importance for higher θ_D. The condition $\theta_D < 3T'/2$ is usually fulfilled at $T' = 298$ K, but not in compounds with low atomic masses (such as LiF) or in compounds with strong interatomic forces (e.g., covalent bonding). Such systems are implicitly excluded in Latimer's work [2], which refers to ionic compounds and has a remark that the heat capacity should have reached its classical Dulong–Petit value (equivalent to $\theta_D \lesssim T'$).

The invariance of the interatomic forces is only approximately fulfilled. In his improved version [3], Latimer allowed for this when he let the entropies of the negative ions vary with the charge of the positive ion in the compound. He also changed Eq. (1) slightly to account for ionic size effects. It is intuitively clear that if certain ions in a compound are replaced by smaller ions, the latter will be more loosely bound to their equilibrium positions, resulting in a reduced β. The trend is opposite if the replacement is by large ions.

Latimer [3] treated negative ions with several atoms (e.g., SO_4^{2-}) in the same way as monatomic ions. This is correct provided that the ion with several atoms vibrates approximately as a single mass. Then one should use the total ion mass for M_i in Eq. (6).

4. DISCUSSION

We have seen that the ion masses M_i enter in a unique way, as $\log M_e$, in the leading high temperature term for the entropy. An additional dependence on M_i, such as that assumed by Latimer [3], Treadwell and Mauderli [5], and Kelley [7], represents an empirical way to fold force constant changes into mass dependent terms. It is the correlation between ion size and ion mass which makes this feasible.

There is empirical evidence that the variation of the interatomic forces can be accounted for if β is made a function of the molar volume V of the compound. Cantor [10] argued, with reference to a Debye model and dimensional analysis, that β should scale as $V^{-1/3}$. Grimvall and Rosén [11] noticed the same behavior in a related analysis for alkali halides. However, it must be stressed that there is no reason to assume a particular universal power law in V for the scaling of β. For instance, when the analysis in ref. [11] is repeated for some compounds of the type AB_2 ($PbCl_2, PbBr_2, PbI_2, CuCl_2, TiCl_2, MgCl_2$), it is found that β scales approximately as $V^{-2/3}$. Latimer's rule gives S^0 with fair accuracy, but there is a related procedure, developed by Grimvall and Rosén, which should be more accurate for the estimation of an unknown entropy when the entropy of chemically similar compounds are known. The reader is referred to ref. [11] for details.

5. CONCLUSIONS

In the literature several empirical expressions are found which relate the standard entropy S^0 of a compound to the masses of the constituent atoms or to the total molecular weight. In particular, Latimer assigns entropy contributions to each atom which vary with their mass M as $\ln M$.

It is shown from lattice dynamical theory that Latimer's functional dependence correctly expresses the explicit mass dependence of the entropy at high temperatures.

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